2

AD-A237 884

REPORT DOCUMENTATION PAGE

JUL 1 0 1991

1a	1b RESTRICTIVE MARKINGS NA
2a SECURITY CLASSIFICATION AUTHORITY U	3 DISTRIBUTION/AVAILABILITY OF REPORT Distribution Unlimited
2b DECLASSIFICATION/DOWNGRADING SCHEDULE NA	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) NA	5 MONITORING ORGANIZATION REPORT NUMBER(S) NA
6a NAME OF PERFORMING ORGANIZATION University of Utah 6b OFFICE SYMBOL *(If applicable)*	7a NAME OF MONITORING ORGANIZATION ONR
6c ADDRESS *(City, State, and ZIP Code)* Department of Physics University of Utah Salt Lake City UT 84112	7b ADDRESS *(City, State, and ZIP Code)* Office of Naval Research, Code 114ss 800 North Quincy Street Arlington VA 22217
8a NAME OF FUNDING SPONSORING ORGANIZATION ONR 8b OFFICE SYMBOL *(If applicable)*	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-90-J-1841
8c ADDRESS *(City, State, and ZIP Code)* Office of Naval Research, Code 114ss 800 North Quincy Street Arlington VA 22217	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO: 63222C PROJECT NO: TASK NO: WORK UNIT ACCESSION NO:

11 TITLE *(Include Security Classification)*

(U) Research in the Physical Science with Application to the Free Electron Laser

12 PERSONAL AUTHOR(S)

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT *(Year, Month, Day)*	15 PAGE COUNT
Final Technical	FROM 1/90 TO 12/90	1991, July 3	23

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18 SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
FIELD	GROUP	SUB-GROUP	

19 ABSTRACT *(Continue on reverse if necessary and identify by block number)*

The goals of this research are to perform research in the physical sciences (chemistry, electrical engineering, materials science, physics) with direct application to Free Electron Laser technology. Recent progress includes: (1) photoluminescence excitation (PLE) spectroscopy on thin films using a free electron laser (FEL), (2) optical properties of ordered and partially ordered GaInP alloys, (3) Raman scattering in GaInAs/InP quantum wells, (4) diffusion in the GaAs/AlGaAs system, (5) GaInP/AlGaInP strained quantum wells, (6) photochemical chain reactions in olefins, (7) photopolymerization of acetaldehyde, (8) resonant Raman scattering of polydiacetylene, (9) spectral hole burning of CN^- in cesium halides, (10) transient photoinduced resonant Raman scattering in polyacetylene, and (11) theory of anharmonic processes in disordered solids.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	U

22a NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE *(Include Area Code)*	22c OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Final Technical Report

on

RESERACH IN THE PHYSICAL SCIENCES WITH APPLICATION TO THE FREE ELECTRON LASER

(N000-14-86-K-0710)

Time Period: 5/86 - 12/89

P.C. Taylor, Department of Physics

G.B. Stringfellow, Department of Materials Science and Engineering

R.E. Benner, Department of Electrical Engineering

R.M. Cohen, Department of Materials Science and Engineering

C.A. Wight, Department of Chemistry

F. Luty, Department of Physics

W. Gellermann, Department of Physics

Z.V. Vardeny, Department of Physics

D.C. Mattis, Department of Physics

University of Utah
Salt Lake City UT 84112

Table of Contents

Final Report for the ONR FEL Contract No. N00014-90-J-1841
1/1/90 - 12/31/90
P.C. Taylor
Department of Physics
University of Utah

SEMICONDUCTINHG LAYER STRUCTURES, QUANTUM WELLS AND SUPERLATTICES

A. Optical Properties

Abstract

The first photoluminescence excitation (PLE) spectroscopy measurements using a free electron laser (FEL) have been performed on thin films of hydrogenated amorphous silicon (a-Si:H). The high power and tunability of the FEL has allowed measurements of the PLE well below the optical absorption edge in this thin film amorphous semiconductor. This method should be useful for probing below-gap absorption mechanisms that contribute to PL in a wide class of semiconducting thin films. The excitation intensity dependence of the photoluminescence (PL) from $Ga_{0.52}In_{0.48}P$ grown by organometallic vapor phase epitaxy on GaAs substrates has been investigated as a function of epitaxial layer growth temperature and substrate orientation. It is well known that the degree of ordering and the band-gap energy of this material are functions of growth conditions. We have found a PL emission which shifts rapidly with excitation intensity. The rate of emission shift is also a function of growth conditions including substrate orientation. There is, however, no significant correlation between the band-gap energy and the rate of emission shift in $Ga_{0.52}In_{0.48}P$. This PL shift is explained in terms of band filling of potential fluctuations that are associated with a microstructure consisting of ordered domains within a disordered matrix.

Progress

There exists a characteristic photoluminescence (PL) peak at 0.8 eV in a-Si:H whose intensity scales with the silicon dangling bond density as measured by electron spin resonance. For this reason, among others, the PL at 0.8 eV has been attributed to this silicon dangling bond defect, and the most common interpretation of the radiative transition is between an occupied localized state at the edge of the conduction band and a singly occupied silicon dangling bond.

In addition to the PL band at 0.8 eV, there also exists a PL band that peaks at 1.2-1.4 eV. In good, device-quality films of a-Si:H it is the latter peak that dominates the PL processes at low temperatures. This higher-energy peak is usually interpreted as due to recombination of electrons in localized conduction band tail states with holes in localized valence band tail state.

The excitation spectrum for PL at 0.8 eV and obtained on a-Si:H with an FEL has two distinguishing features, an exponential rise at lower energies followed by a leveling off above ~ 1.15 eV. Although the precise functional form of the data at low energies is not uniquely determined, the data are consistent with an exponential rise whose slope is the same as that measured in optical absorption at higher energies.

For optical excitation at energies below the band gap a different absorption process is required. Because the energies are too small to excite directly across the gap with any efficiency, excitation through the manifold of dangling bond defect states is necessary. These absorption processes, in general, involve two steps and as such should be expected to show a superlinear dependence on excitation intensity. In fact, in experiments performed with a cw YAG laser at 1.17 eV the PL above 1.2 eV is observed with a superlinear power dependence that demonstrates the two-step excitation process. Because the dangling bond states have a finite

density ($\sim 10^{15}$ cm^{-3}), the PL that results from two-step excitation processes that proceed through these states should be expected to become linear in excitation intensity at high powers. This dependence at high powers is expected because the excitation into the existing defect states saturates. This saturation is observed in the FEL experiments.

The ternary semiconductor $Ga_{0.52}In_{0.48}P$, with a band gap of 1.9 eV and a lattice constant equal to that of GaAs, is an attractive alternative to AlGaAs. For example, it has been shown that the $Ga_{0.52}In_{0.48}P$/GaAs heterointerface exhibits a surface recombination velocity of less than 2 cm/s, or almost two orders of magnitude less than the typical AlGaAs/GaAs interface. However, $Ga_{0.52}In_{0.48}P$ is a complex material that is not well understood. Specifically, it has been reported that the band-gap energy E_0 of $Ga_{0.52}In_{0.48}P$ grown by organometallic vapor phase epitaxy (OMVPE) can vary by 70-100 meV for growth temperatures in the range of 600-725°C[2]. E_0 is also a function of substrate orientation and vapor phase chemistry. A similar variation of the critical point, E_1, has also been measured with electroreflectance. It has also been reported that $Ga_{0.52}In_{0.48}P$ orders on the Group III sublattice, with a CuPt-like structure. This ordered structure is predicted to have a bang-gap energy less than that of the random alloy. Therefore, it would be plausible that the extent of such ordering, as measured by the long-range order parameter, should correlate with the band gap. One group finds this correlation and two groups do not. Part of the problem is related to the observation that the ordering in $Ga_{0.52}In_{0.48}P$ is not perfect nor homogeneous, but rather consists of a composite of partially ordered domains in a disordered matrix. We have examined the excitation intensity dependence of the PL in $Ga_{0.52}In_{0.48}P$, and shown that it is affected by the same parameters that affect the band gap and ordering.

We have observed large PL peak shifts with excitation intensity in $Ga_{0.52}In_{0.48}P$ grown by OMVPE. The effect is most pronounced at T_g = 650°C in samples grown on singular (100) GaAs substrates or those oriented 2° off (100) toward (110) and cannot be explained by the conventional treatments of the Coulombic interaction between donor-acceptor pairs or statistical alloy fluctuations. We argue that the shift is due to potential fluctuations and that these fluctuations are a consequence of the existence of ordered domains within a disordered matrix.

It is reasonable to expect that potential fluctuations could result from the composite structure of $Ga_{0.52}In_{0.48}P$ consisting of low band gap, ordered domains in a high band gap, disordered matrix. From band-filling arguments, the emission shift rate should depend on the depth of the potential well (i.e., the degree of order within the ordered domain), and the size and density of the ordered domains. Although it is difficult to measure these parameters in all the $Ga_{0.52}In_{0.48}P$ samples, some correlations between the emission shift rate and the microstructure $Ga_{0.52}In_{0.48}P$ can be made. At the two growth temperature extremes, the emission shift rate is relatively small and the band-gap energy is high. From transmission electron diffraction (TED) studies we know that the volume density of ordered domains is less than 1% for the samples grown at 600°C and about 30% for samples grown at 740°C. The low density of domains may account for the small emission shift for the samples grown at low temperatures. On the other hand, the high band gap of the samples grown at 740°C, implies that the potential well depth associated with the ordered domains is relatively shallow (due to a relatively low degree or ordering within the domains). For intermediate growth temperatures, the emission shift rate is a strong function of the substrate misorientation, whereas the band gap is only a weak function of the same. This would imply that the potential depth of the ordered domains is roughly the same for the two substrate orientations, but the size and/or density are not. However, using TED we have not been able to confirm this supposed difference in microstructure for $Ga_{0.52}In_{0.48}P$ grown on the two different substrates.

Publication Acknowledging ONR Support

1. J. Ristien, B. Hooper and P.C. Taylor, J. Opt. Soc. Am. **B6**, 1003 (1989).

2. T.Y. Wang, G.B. Stringfellow, Z.H. Lin and P.C. Taylor, J. Vac. Sci. and Technol. **B7**, 4 (1989).

3. T.Y. Wang, Z.H. Lin, G.B. Stringfellow and P.C. Taylor, J. Vac. Sci. Technol. **B7**, 824 (1989).

4. J. Ristein, B. Hooper, S. Gu and P.C. Taylor, Solar Cells 27, 403 (1989).

5. M.C. DeLong, J.M. Olson and P.C. Taylor, J. Vac. Sci. Technol. B8 948 (1990).

6. M.C. DeLong, J.M. Olson and P.C. Taylor, Appl. Phys. Lett. 57, 620 (1990).

Final Report for the ONR FEL Contract No. N00014-90-J-1841
1/1/90 - 12/31/90
R.E. Benner and G.B Stringfellow
Departments of Electrical Engineering and Materials Science and Engineering
University of Utah

SEMICONDUCTING LAYER STRUCTURES, QUANTUM WELLS AND SUPERLATTICES

B. Raman Scattering from GaInAs/InP Quantum Wells

Abstract

Raman spectra have been obtained from thin GaInAs/InP quantum wells, both lattice matched and strained, including GaAs/InP and InAs/InP quantum wells, grown by organometallic vapor phase epitaxy (OMVPE). Features in the Raman spectra associated with neither the GaInAs well nor the InP barriers have a relatively constant intensity for decreasing well width for all the samples. These features also have the same energies for both the lattice-matched and the strained-layer samples. This behavior is consistent with a graded interfacial region of InAsP between the well and the barriers. Raman spectra from a series of GaInAs/InP quantum wells grown with different growth interruptions indicate the existence of the interfacial layer is dependent on the use of growth interruptions.

Longitudinal optic (LO) modes are shown to be screened by the presence of free carriers. This is demonstrated with Raman spectra from heavily doped GaAs. This same effect is seen in quantum well samples in which the GaAS-like LO mode associated with the well is screened by photogenerated carriers collected by the well.

Progress

A variety of optical techniques including photoluminescence, photoluminescence excitation, spectroscopic ellipsometry, and Raman scattering have been used to characterize the GaInAs/InP system. Anomalies in the results of these studies have indicated that in some GaInAs/InP wells the interfaces between the two materials are not abrupt, but have an interfacial layer of $InAs_xP_{1-x}$ between the active GaInAs region and the barrier InP region. Spectroscopic ellipsometry has directly indicated that such an interfacial region exists, and Raman scattering and photoluminescence have given somewhat less conclusive evidence.

We have completed a Raman scattering study aimed at identifying the interfacial layers in GaInAs/InP structures grown by OMVPE.

The collection of data was accomplished using a multichannel CCD array as a detector. The effectiveness of data collection using different scan parameters for the detector was investigated. It was found that by binning the CCD, the signal-to-noise ratio could be greatly increased, while keeping relatively short integration times.

A series of thin GaInAs/InP, GaAs/InP and InAs/InP wells were studied. In the spectra from all these wells, peaks corresponding to $InAs_xP_{1-x}$ were seen. In addition, a series of thin wells grown with different growth interruptions shows the presence or absence of these peaks depends on the use of growth interruptions. Corresponding shifts in the PL spectra of these samples have also been seen. These results appear to confirm the fact that there is a thin interfacial layer of InAsP in these wells which can have a large effect on the properties of very thin wells.

Using different polarization orientations of incident and scattered light, Raman spectra were taken from bulk $Ga_{0.47}In_{0.53}As$ to show that $Ga_{0.47}In_{0.53}As$ has only one phonon mode with LO characteristics. A series of doped samples of GaAs was studied, and it was demonstrated that high free carrier concentrations in a material could screen the electron-phonon interaction in the material; i.e., for the scattering geometry used, the LO phonon could be effectively screened. This same effect was then demonstrated in thin semiconductor quantum wells and offered as a possible explanation for the reduction of the single GaAs-like LO peak in thin GaInAs/InP quantum wells, and as an explanation why the intensity of the GaAs-like LO peak does not decrease proportionally to decreasing well width.

Publications Acknowledging ONR Support

1. John L. Huber, "Raman Scattering from GaInAs/InP Quantum Wells," Master's Thesis, University of Utah, 1990.

Final Report for the ONR FEL Contract No. N00014-90-J-1841
1/1/90 - 12/31/90
R.M. Cohen
Department of Materials Science and Engineering
University of Utah

SEMICONDUCTING LAYER STRUCTURES, QUANTUM WELLS AND SUPERLATTICES

C. Diffusion

Abstract

Thermodynamic principles have been applied to diffusion and interdiffusion in GaAs and AlGaAs in order to explain the dependence of diffusion on the Fermi level and As overpressure. The resulting model describes a wide range of observed results in terms of a charged group III vacancy and interstitialcy (kick-out) mechanism.

Progress

An analysis of diffusion, performed under near-equilibrium conditions, in GaAs and AlGaAs has shown that diffusivity is expected to be an explicit function of three thermodynamic variables: temperature, Fermi level, and As overpressure. These three variables directly control the concentration of charged point defects, (e.g., vacancies and interstitials) in different ways, and thus they can enhance or retard the rate of diffusion. The rate of interdiffusion in GaAs-AlGaAs superlattices is known to exhibit a V-shape dependence upon As overpressure. These observations strongly suggest that a vacancy mechanism dominates at high overpressures while an interstitialcy mechanism dominates at low overpressures. Since the concentration of charged point defects depends upon the Fermi level, changes in group m interdiffusion as a function of Fermi level can be used to infer the charge state of the defect. Experimental results reported by several groups are reasonably consistent and they indicate that the Ga vacancies have a charge state of -3 and the Ga interstitials have a charge state of +2, in n- and p-type GaAs, respectively. It is worth noting that these experimental results are consistent with the first principles calculations of Baraff and Schluter.

Publications Acknowledging ONR Support

1. R. M. Cohen, "Application of the charged point defect model to diffusion and interdiffusion in GaAs", J. Appl. Phys. **67**, 7268 (1990).

2. R. M. Cohen, "Ga self-diffusion in GaAs", accepted in J. Electron. Mater., tentatively for 6/91.

Final Report for the ONR FEL Contract No. N00014-90-J-1841
1/1/90 - 12/31/90
G.B. Stringfellow
Department of Materials Science and Engineering
University of Utah

SEMICONDUCTING LAYER STRUCTURES, QUANTUM WELLS, AND SUPERLATTICES

D. Growth and Characterization

Abstract

GaInP/AlGaInP strained single and multiple quantum wells grown by organometallic vapor phase epitaxy (OMVPE) were studied in great detail using optical techniques as well as by electron microscopy. The shift of the peak position with well width and composition was found to be accurately described using model solid theory calculations. The fundamental optical properties of a new III/V alloy, InPSb, were also studied.

Progress

GaInP/AlGaInP Quantum Wells

The organometallic vapor phase epitaxy (OMVPE) technique has been used to produce $Ga_{0.4}In_{0.6}P/Al_{0.2}Ga_{0.3}In_{0.5}P$ strained single and multiple quantum well structures. This work represents some of the first work demonstrating abrupt interfaces as characterized by the low-temperature photoluminescence (PL), thermally modulated photoluminescence (TMPL), photoreflectance (PR), and PL excitation (PLE) spectroscopies.

The growth was carried out in a horizontal, infrared-heated, atmospheric pressure OMVPE reactor. The use of interruptions was optimized to give the sharpest low temperature PL spectra.

The effect of changing the interrupt time for single quantum wells was mainly to change the PL intensity, presumably due to oxygen contamination of the interface. The peak position was not a function of interrupt time. The band lineups at the GaInP/AlGaInP interface were analyzed using the model solid theory. Using the results, the experimental PL peak energy versus well width has been accurately described. The results obtained by others for lattice-matched quantum wells are also accurately described using this model.

Twenty layer multiple quantum wells have also been grown. The x-ray diffraction satellite peaks and narrow PL half-width indicated that the strained quantum wells are of high quality and that the composition and thickness are under precise control.

Optical Studies of Novel III/V Alloys

A new III/V alloy, $InP_{1-x}Sb_x$ was produced using OMVPE. The first reliable determination of the energy band gap versus solid composition was obtained using optical absorption measurements. The bowing parameter for the direct band gap was determined to be 1.52 eV.

Publications Acknowledging ONR Support

1. T.Y. Wang, A.W. Kimball, G.S. Chen, D. Birkedal and G.B. Stringfellow, GaInP/AlGaInP Strained Quantum Wells Grown Using Atmospheric Pressure OMVPE, J. Crystal Growth **109**, 285 (1991).

2. E.H. Reihlen, M.J. Jou, Z.M. Fang, and G.B. Stringfellow, Optical Absorption and Emission of InPSb Alloys,, J. Appl. Phys. **68** 4604 (1990).

3. T.Y. Wang, A.W. Kimball, G.S. Chen, D. Birkedal, and G.B. Stringfellow, Atmospheric Pressure OMVPE Growth of GaInP/AlGaInP Strained Quantum Wells, J. Appl. Phys. **68**, 3356 (1990).

Final Report for the ONR FEL Contract No. N00014-90-J-1841
1/1/90 - 12/31/90
C.A. Wight
Department of Chemistry
University of Utah

PHOTOCHEMICAL AND PHOTOPHYSICAL PROCESSES IN THIN FILMS AND ON SURFACES

A. Photopolymerization and Chain Reactions

Abstract

We have recently extended our studies of photochemical chain reactions in disordered solids to include chlorination of methylcyclopropane, ethylene, and propylene, as well as the photopolymerization of acetaldehyde.

Progress

Our recent investigation of the methylcyclopropane reaction was revealing from a mechanistic standpoint. These reactions are carried out by depositing a binary solid solution of the hydrocarbon with molecular chlorine onto the surface of an optical window. Chain reactions are initiated by UV laser photolysis of the chlorine component. Product identification and photochemical quantum yields are determined by transmission FTIR spectroscopy of the solid films. In this particular reaction several possible products were postulated, but only one pathway observed: formation of chloromethylcyclopropane. This result means that activation of the methyl hydrogen atoms in this system by the strained ring provides a low-energy pathway from reactants to products. Steric constraints presented by surrounding molecules in the low-temperature (30-77 K) solid do not provide a viable mechanism for forming other products by higher energy reaction paths.

The reaction of chlorine with simple olefins is an extension of our previous work on cyclopropane, where we found that the formation of conformationally pure reaction products gave unambiguous information about the stereochemistry of a solid state reaction. In the case of ethylene and propylene, the reaction products correspond to addition of molecular chlorine across the carbon-carbon double bond of the olefin. In liquid solutions, it is known from stereochemical studies involving formation of optically active products that addition of the two chlorine atoms occurs from opposite sides of the molecular plane. However, the steric constraints of the solid state make it unlikely that such *trans*-addition to the double bond could occur in the solid state. This would tend to favor a *syn*-addition mechanism.

We reasoned that *syn*-addition would lead to formation of the *gauche* conformer of the dichloroalkane product in each case, while *trans*-addition would form the *anti* conformer. The product conformers are distinguishable by their IR absorption spectra in the C-Cl stretching region near 700 cm^{-1}. We carried out several experiments on both compounds and found that the chain reaction of chlorine produces predominantly the *gauche* conformer in each case. From a mechanistic viewpoint, this means that the two chlorine atoms in each molecule of dichloroalkane originate in different chlorine molecules in the reactive solid! Our measurements of the photochemical quantum yields of these reactions provide good evidence for long chains in this type of reaction (in excess of 100 product molecules formed per Cl atom pair formed by the UV photolysis laser).

Experimental investigation of the solid state polymerization of acetaldehyde reveals that the oligomer chain lengths are modest (about 5-7 monomers incorporated per chain reaction initiated by UV photolysis). These results are quite similar to the results obtained for photopolymerization of solid formaldehyde monomers

in a disordered solid solution, and provide support for our previous interpretation of the mechanism of that reaction.

Publications Acknowledging ONR Support

(none)

Final Report for the ONR FEL Contract No. N00014-90-J-1841
1/1/90 - 12/31/90
R.E. Benner and Z.V. Vardeny
Departments of Electrical Engineering and Physics
University of Utah

PHOTOCHEMICAL AND PHOTOPHYSICAL PROCESSES IN THIN FILMS AND ON SURFACES

B. Resonant Raman Scattering Studies of Disorder in Solution-cast Polydiacetylene Films

Abstract

The disorder in polydiacetylene films cast from solution was studied by Raman scattering under preresonance and resonance conditions in both Stokes and anti-Stokes configurations. The disorder-induced inhomogeneities in the exciton levels and the strongly coupled vibrations cause strong dispersion of the C=C and C≡C stretching frequencies with the laser excitation photon energy, surprisingly similar to that of trans-polyacetylene. We found, however, that the complete inhomogeneously broadened phonon distribution is revealed when the excitation is not in resonance. In addition to the excitation resonance, resonances associated with the Stokes and anti-Stokes emission beams strongly affect the measured Raman profiles.

Progress

We have developed the capability of performing cw Raman scattering measurements with excitation wavelengths varying from the uv to the near-infrared using a combination of argon, argon-pumped dye, and argon-pumped Ti:sapphire lasers. Both a conventional single channel spectrometer system with a photomultiplier detector and an optical multichannel spectrograph system with a cooled CCD detector are available for Raman data acquisition. The equipment allows us to perform cw resonance Raman scattering (RRS) studies in a variety of materials including thin films. In addition, the optical multichannel detection system can be used in a pump-probe configuration for picosecond time-resolved Raman studies.

RRS is an efficient method for studying disorder in conducting polymers since the inhomogeneously broadened distribution of phonon frequencies caused by the disorder is selectively probed by changing the excitation laser photon energy. The resonant enhancement causes the frequencies of the most strongly coupled Raman-active phonons to shift with excitation frequency; this phenomenon is known as phonon dispersion.

The RRS dispersion in polyacetylene [$(CH)_x$] has been the focus of experimental and theoretical studies for the last decade because of the relative simplicity of the polymer backbone structure, the measured large phonon dispersion, and the convenient laser excitation range (in the visible and near uv spectrum). Two competing models, an heuristic distribution of chain lengths and the amplitude modes model, can explain well the RRS dispersive spectra in various isomers and doped forms of $(CH)_x$. Recently, a successful attempt was made to unify these two theories into a single model. It is now generally believed that the electron interactions and consequently the energy gap in $(CH)_x$ are dominated by the electron-phonon (*e-p*) coupling and that the disorder in the films causes an inhomogeneous distribution of the *e-p* coupling through a distribution of conjugation lengths. Polydiacetylene (PDA), on the other hand, is believed to be dominated by stronger electron-electron (*e-e*) interactions. A comparison between the RRS dispersion in PDA and that of $(CH)_x$ may reveal new information on the relative importance of these interactions. Also PDA exhibits exceptional electronic and optical properties which include high nonlinear optical constants and strong exciton-phonon coupling; both properties stem from the strong one-dimensional anisotropy of this material. Moreover, optical-

quality PDA thin films can be easily prepared by the technique of spin casting from solution, and PDA is also the first conjugated polymer to form a real all-optical device.

Our RRS studies of the disorder in PDA (4-BCMU) films show that under resonant conditions, the Stokes (S) as well as the anti-Stokes (AS) Raman frequencies of the C=C and C≡C stretching vibrations exhibit strong dispersion with ω_L surprisingly similar to that in *trans*-$(CH)_x$. We also show that the complete disorder-induced phonon distribution is directly revealed when ω_L is not in resonance. By measuring the S to AS intensity ratio as a function of ω_L, we demonstrate the importance of the resonance enhancement with the scattered (outgoing) beam; this effect has not been taken into account in any of the existing theories concerning RRS dispersion in conducting polymers.

The similarity with *trans*-$(CH)_x$ may indicate that the same type of disorder exists in both materials. Since the interaction parameters ultimately depend on the conjugation length N, we believe that a distribution of conjugation lengths is the underlying mechanism for the RRS dispersion in both PDA and $(CH)_x$. In PDA it causes inhomogeneity in the exciton energies E_x, in $(CH)_x$ it is E_g which varies with N. More theoretical work is needed to elucidate these points.

In summary, we have investigated RRS in PDA 4-BCMU films cast from solution. The disorder-induced distributions in the exciton levels and the C=C and C≡C stretching vibrations cause strong dispersion of these phonon frequencies with ω_L in both S and AS configurations. We showed, however, that a single experiment, when ω_L is not in resonance, reveals the complete inhomogeneous broadened phonon distribution and can serve as a standard method to probe the amount of disorder in PDA films. We have also demonstrated the importance of resonances with the outgoing (scattered) beams for both S and AS configurations. Finally, we have demonstrated the similarity in the types of disorder in PDA and *trans*-$(CH)_x$.

Publications Acknowledging ONR Support

1. L.X. Zheng, R.E. Benner, Z.V. Vardeny, and G.L. Baker, "Resonant Raman Scattering Studies of Disorder in Solution-Cast Polydiacetylene Films, Physical Review B, Rapid Communications, 42 (1990) 3235.

Final Report for the ONR FEL Contract No. N00014-90-J-1841
1/1/90 - 12/31/90
F. Luty and W. Gellermann
Department of Physics
University of Utah

IONIC SOLIDS AND TUNABLE INFRARED LASERS

Abstract

We applied a narrow-linewidth single-mode tunable color center laser system for spectral hole-burning investigations of the vibrational absorption of CN^- molecules in various ionic host crystals. For orientationally aligned CN^- defects in cesium halides, persistent spectral holes and antiholes could be obtained at temperatures $T \leq 40K$. Hole and antihole formation properties can be understood in a model in which the CN^- molecules performs 180 degree orientational flips under repeated optical excitation. For dilute defect systems in CsCl, minimum homogeneous linewidths of $\sim$ 10 MHz were measured, indicating the existence of rapid dephasing processes. In the regular sublattice of pure alkalicyanides (antiferroelectrically ordered in KCN, and electrically disordered in RbCN), persistent vibrational holeburning, vibrational energy transfer, and anti-hole formation have been studied. In our extended investigation of electron-vibration energy transfer from optically excited F centers into molecular defects of ionic crystals, we studied with optical absorption and magneto-optical (MCD) techniques F-center/OH^- defect pairs in cesium halides. Spin-lattice relaxation and spin-orbit coupling has been determined and compared to theoretical models. Moreover, the spin-memory loss in the optical excitation cycle was measured to determine its possible correlations to the E-V transfer process in this cycle. In our efforts to develop new color center lasers, we realized mode-locked $KCl:Na^+:O_2$ color center laser operation with nearly transform limited $\sim$5-10 psec wide pulses throughout a 1.73-2.10 μm tuning range. This new laser provides a high average power picosecond light source in a wavelength region where only few competing laser systems exist.

Progress

Persistent spectral holeburning in solids has gained considerable interest in the last decade partially due to its potential technological application in optical information storage systems. Beyond that, it is a powerful tool in high-resolution spectroscopy since it has the capability to measure the intrinsic homogeneous absorption profiles of absorbers in the presence of line-broadening extrinsic perturbations. Since the homogeneous linewidth is inversely proportional to the dephasing time T_2 of the excited state, information can be obtained in general on the dynamics of the absorber/host coupling.

Most of the previous work in holeburning spectroscopy has been done on electronic transitions in the visible range (which is largely due to the availability of tunable laser sources in that range), and vibrational transitions, occurring predominantly in the IR, have received only very little attention.

We have started to investigate the existence and properties of persistent spectral holes in the inhomogeneously broadened vibrational transitions of CN^- molecular defects in cesium halides. These materials have recently gained interest due to their vibrational optical emission and laser properties. As the first system for our holeburning experiments we used orientationally aligned CN^- defects, consisting of a CN^- ion associated to a neighboring alkalineion impurity (K^+ and Rb^+), existing in two different ionic configurations with slightly different transition energies depending on whether the C or N molecular end of the molecule is opposite the neighboring impurity ion. In order to test the ionic configuration model and to study the dynamic properties of these defect-pairs, hole burning experiments were performed. For excitation we used a single-mode color center laser system which could be tuned over the 2nd harmonic transitions of the studied defects near

4000 cm^{-1}. Narrow persistent spectral holes and antiholes could be burned into both transitions of $CN^-:K^+$ and $CN^-:Rb^+$ defect pairs in CsCl, CsBr, and CsI hosts at temperatures $T \leq 40$ K. Using oriented crystals and polarized excitation, the underlying holeburning and antihole formation mechanism could be identified as light-induced 180° orientational dipole flips of the CN^- molecule, and the previously assumed <111> orientation of the defects could be confirmed. A minimum homogeneous linewidth of ~10 Mhz, corresponding to a dephasing time $T_2 \sim 15$ nsec was obtained in CsCl. Compared to the radiative lifetime T_1 of the molecules this value is ~6 orders of magnitude smaller. We found that the fast dephasing is caused by rotational motion and "stress-modulation" from isolated CN^- molecules which are always present in addition to the aligned defects in the crystal.

Using the same single mode tunable color-center-laser for excitation and as a high-resolution spectrometer, holeburning studies have been performed at 4 K in the 2nd harmonic CN^- vibrational absorption of pure alkali-cyanides around 4000 cm^{-1}. In antiferroelectrically ordered KCN, a large number of sharp (~10^{-3} cm^{-1}) holes can be burned persistently in the 1 cm^{-1} broad absorption bands of the four CN^- isotopes. Spectrally selected CN^- dipoles (aligned in the ~10^7 V/cm mean crystal field) disappear under excitation producing holes with an efficiency of ~10^{-3}, and reappear as "anti-hole absorption" at about 10 cm^{-1} higher frequency: new oriented opposite to the mean field. Besides this "direct" process, the primary localized excitation can diffuse spectrally and spatially by V-V energy transfer through the CN^- sublattice, producing "indirect" molecular reorientations on its path of migration. The formation of the (broad) hole component caused by this process could not be observed on the existing strong absorption backgrounds, while a build-up of the 10 cm^{-1} shifted anti-hole absorption on zero background can easily be detected: either in the isotope system under optical excitation, and/or in the isotopes of smaller eigenfrequencies (down to $^{13}C^{15}N$), where the migrating excitation-energy can be trapped. In antiferroelastically ordered but electrically disordered RbCN, many sharp, persistent, and 100% deep holes can be burned. Anti-hole absorption build-up, which is not spectrally separated, but spread over the whole absorption band due to the random "electric dipole glass" field in the crystal, cannot be detected.

Electron-vibration (E-V) energy transfer from optically excited F centers into neighboring OH^- or CN^- molecular defects is alkali-halides is under extensive study. We measure and analyze the achieved population of CN^- vibrational V-states either by a cascade of slow (msec) vibrational fluorescence processes or by anti-stoke resonance Raman scattering. Population inversion of the V-levels achieved in this E-V transfer process has already produced the first model cases of visible-light-pumped vibrational lasers in CsCl and CsBr hosts.

The behavior of the F center spin in the optical excitation and energy-transfer cycle is of particular importance. First, we have studied the spin-orbit (SO) structure of F center OH^- pairs in CsCl, CsBr and CsI by magnetic circular dichroism (MCD) measurements. This system is of interest because it combines the strong SO effect of the F center in cesium halides with the exceptionally large splitting (0.7 eV) of the electronic absorption bands caused by the associated OH^- molecule. The spectral shape and temperature behavior of the MCD confirm that the $F_H(OH^-)$ center consists of an F center strongly perturbed by an OH^- molecule on a <100> next nearest neighbor position. From these MCD results the SO parameters Δ have been determined for $F_H(OH^-)$ and compared to that of pure F centers using the Henry, Schnatterly, Slichter moment method. Due to their C_{4v} symmetry $F_H(OH^-)$ centers yield two different spin-orbit parameters Δ_2 and Δ_{12}, which turn out to be close to the values of the F center in all three hosts. This is in contrast to the strong influence the association of the OH^- molecule has on other electronic properties.

A new defect type consisting of an F center attached to a pair of OH^- molecular ions has been found in highly OH^- doped CsCl and CsBr. Its formation kinetics is based on optically induced F- center migration with primary association to single OH^- ions, followed under prolonged irradiation by their bleaching and F center association to OH^- ion pairs. When performed with polarized light, this process produces linear dichroism by selective polarized bleaching, indicating <100> symmetry of the new complex. The two attached OH^- defect ions split the F band into ~1 eV separated absorptions polarized parallel and perpendicular to the <100> axis of the complex, a splitting unique in size among all F aggregate centers. Spectral and temperature dependence

of magnetic circular dichroism measurements and the derived negative spin-orbit parameter confirm uniaxial symmetry and one-electron perturbed F center character of this new defect.

Besides the spin-lattice relaxation time of the electronic ground state, the spin-memory loss ε, i.e., the probability of spin-flip during a complete electronic excitation and relaxation cycle, has been measured with MCD techniques at 4K. The main result is a strong increase of the spin-memory loss ε for $F_H(CN^-)$ in CsCl and CsBr compared to F centers, while ε remains nearly unchanged (only a slight decrease) for $F_H(OH^-)$ centers in KCl and KBr. Attempts are under way to explain these spin-memory loss results in correlation to the electron relaxation and e-v energy transfer processes occurring in the same optical cycle.

Concerning our color center laser development efforts we investigated the potential $F_2{}^+$-like color centers in KCl:Na^+:O^- crystals for mode-locked laser operation. The high optical gain cross section (σ_0 = 1-2 $\times$ 10^{-16} cm^{-3}) and the long fluorescence decay time (100 nsec $\leq \tau \leq$ 200 nsec) are characteristics which make these color centers an excellent candidate for efficient mode locking via synchronous pumping with a mode locked pump laser. Since the fluorescence time is long compared with the time between consecutive pump pulses T_{RT} (typically 10 nsec), the material fulfills the conditions for a synchronous mode-locking regime where the equilibrium gain is nearly constant between consecutive pulses. In this case theory predicts pulses of $sech^2$ shape, which in peak intensity vary inversely, and in width vary linearly with cavity mismatch; and therefore the pulse energy stays constant. Hence shorter pulses are possible without a loss of energy per pulse. A further consequence is that shorter pulses are expected for higher initial net logarithmic gain, which should be achievable by increasing the pump power.

Pumping the crystals synchronously with ~100 psec 1.32 μm Nd:YAG laser pulses, we could obtain mode-locked color center laser operation with nearly transform limited pulses (~5 to 10 psec) throughout the region 1.73-2.10 μm. The pulses were seen to shorten continuously with increasing pump power levels. At maximum available pump power (2.3 W), average output power up to ~380 mW could be realized in the peak of the tuning range at 1.83 μm. All observed mode locking characteristics were found to be in good agreement with theoretical predictions for a material in which the fluorescence decay time is large compared with the cavity round trip time.

Publications Acknowledging ONR Support

1. M. Schrempel, W. Gellermann, and F. Luty, J. of Luminescence **45**, 313 (1990).

2. M. Schrempel and F. Luty, Intern. Conf. on Dynamical Processes in Excited States of Solids DPC91, Leiden, Netherlands.

3. G. Baldacchini, U.M. Grassano, and F. Luty, Intern. DPC conference 91, Netherlands.

4. V. Dierolf, H. Paus, F. Luty, Phys. Rev B **43**, 9879 (1991).

5. M. Krantz, F. Luty, V. Dierolf, H. Paus, Phys. Rev. B **43**, 9888 (1991).

6. K. Mollmann, F. Mitschke, H. Welling, and W. Gellermann, Proc. Intern. Conf. "Lasers 90," STS Press, McLean, VA 1991.

7. K. Mollmann, F. Mitschke, and W. Gellermann, Optics Commun., 1991, in print. 8. W. Gellermann, J. Phys. Chem. Solids **52**, 249 (1991).

Final Report for the ONR FEL Contract No. N00014-90-J-1841
1/1/90 - 12/31/90
Z.V. Vardeny
Department of Physics
University of Utah

ULTRAFAST AND NONLINEAR SPECTROSCOPY OF SOLIDS

Abstract

We have perfected a novel picosecond transient spectroscopy technique based on photoinduced changes in the Raman scattering spectrum of solids. We named it transient photoinduced resonant Raman scattering (TPRRS) since it involves changes in resonant rather than nonresonant Raman scattering intensity. This technique is suitable for measuring photoexcitation dynamics in solids through the changes in the phonon Raman scattering. It is quite unique among picosecond transient spectroscopies because it enables studies of a single type of photocarriers among all other photoexcitations by following the dynamics of its most strongly coupled phonon mode in the TPRRS spectrum.

We have measured the room temperature photoexcitation dynamics in trans-$(CH)_x$ and in cis and trans segments in 50% partially isomerized $(CH)_x$ in the picosecond time domain by this novel technique of TPRRS. We showed that TPRRS contains considerably more information than transient photoinduced absorption because the decay of individual vibrations in the TPRRS spectrum can be studied separately. This allowed us to study photoexcitation dynamics in cis $(CH)_x$ segments. We observed an exciton migration process from cis segments to the more energetically favorable trans segments within 210 ps.

We also studied picosecond TPRRS in polydiacetylene-4BCMU this films in the Stokes and anti-Stokes configurations. We observed spectral hole burning in both TPRRS and photoinduced absorption (PA) spectra, which lasts only for the time of the cross-correlation between the two picosecond dye lasers. This demonstrates the strong coupling which exists between excitons and phonons in the quasi-1D conducting polymers.

Progress

A. $(CH)_x$

The properties of polyacetylene $(CH)_x$ have been extensively studied in the last decade, in part because it is the simplest of the conducting polymers and hence easiest to compare with model calculations. In particular, it was suggested that the lowest-lying electronic excitations in trans-$(CH)_x$ are topological defects, solitons, with unusual quantum numbers. $(CH)_x$ is unique in that two isomers, cis and trans, coexist in partially isomerized samples before complete isomerization to the more stable trans isomer is achieved by heat treatment at elevated temperatures ($\sim$ 180°C). Contrary to trans, the cis isomer does not support soliton excitations because of lack of degeneracy in its backbone structure. It has been assumed, therefore, that photoexcitations in cis segments are self-trapped singlet excitons and thus quickly recombine accompanied by a moderately strong photoluminescence. Surprisingly, transient PA measurements in partially isomerized $(CH)_x$ samples showed a decay stopping after about 10 ps. To explain this phenomenon it has been suggested that the PA is dominated by photoexcitations in trans segments and consequently the photoexcitation dynamics in cis-$(CH)_x$ has never been measured and thus still remained unresolved.

We introduced a novel technique, the transient photoinduced resonant Raman scattering (TPRRS) with picosecond resolution, in which the transient response of individual resonantly enhanced phonon in the system can be separately monitored. Since the strongly coupled resonant vibrations in cis and trans $(CH)_x$ have

different frequencies and their intensities in RRS can be influenced separately by photoexcitations in cis and trans segments, respectively, then monitoring the TPRRS response of the cis-$(CH)_x$ phonons we could study the photoexcitation dynamics in cis. We indeed observed a faster decay than in trans segments as theoretically predicted, but the reason for it is not faster recombination but a fast migration of photoexcitations from cis into trans segments.

The TPRRS measurements were done with two picosecond dye lasers and the Raman scattering was monitored in the forward configuration by a Raman spectrometer with 3 cm^{-1} resolution, coupled to a multichannel CCD detector. The picosecond set-up consisted of a mode-locked Nd:YAG laser which was frequency doubled and synchronously pumped two dye lasers (pump and probe) producing pulses typically of 2 ps time duration, 0.2 nJ energy at a repetition rate of 76 MHz. The time resolution of the system, as estimated by the dye lasers cross-correlation in KDP, was about 5 ps. The pump and probe beams were focused onto the sample through the sapphire substrate using an achromatic lens and complete overlap was assured by monitoring the PA signal. Measurements were done with different time delay τ between pump and probe. The partially isomerized $(CH)_x$ thin film contained about 50% cis segments and 50% trans segments, as measured by cw RRS.

A single run of TPRRS at a fixed pumped-probe delay τ consisted of collecting four data sets: RRS scattered intensity I_A excited by the pump beam alone, I_B excited by the probe beam alone, I_{A+B} excited by both beams simultaneously and I_C which measured the background spectrum without laser excitation. The TPRRS signal is the change ΔI in the probe RRS intensity I_B induced by the pump beam. ΔI spectrum is then obtained by subtracting $\Delta I = I_{A+B} + I_C - (I_A + I_B)$. For a satisfactory signal to noise ratio, between 4 to 10 runs were averaged out.

The decay of the TPRRS signal can be used to study the photoexcitations population decay processes. The transient dynamics is quite complicated in partially isomerized $(CH)_x$ samples, since with laser excitation $\hbar\omega_L \geq 2.1$ eV, photoexcitations in both cis and trans segments can be generated. However, by separately monitoring the cis and trans resonantly enhanced vibrations using TPRRS spectra at different laser probes, we can separately follow the population decay in both isomers. At 580 nm the cis $(CH)_x$ lines are in full resonance, whereas the trans lines are only in partial resonance. Therefore the 580 nm excitation monitors photoexcitation dynamics mainly in the cis segments. We observed a transient reduction in TPRRS ($\Delta I < 0$) due to photobleaching of the RRS cross section accompanying carrier photogeneration process. By monitoring $\Delta I(t)$ we showed that up to 30 ps the decay kinetics in the cis segments is similar to that of full trans $(CH)_x$ and is due to geminate recombination of the photogenerated singlet excitons. However, at about 30 ps the decay becomes faster indicating that a second decay channel becomes available. This can be more easily observed by pumping at 580 nm and probing at 750 nm, now in full resonance with the trans segments. $\Delta I(t)$ stopped decaying at about 30 ps and contrary to all expectations, started to increase again forming an apparent peak at about 200 ps. We believe that a fast photoexcitation intersystem crossing occurs from cis to trans segments. This is possible since trans segments have lower energy gap ($\sim$ 1.8 eV) compared to that of cis segments ($\approx$ 2.1 eV) and therefore are more energetically favorable. This triggers exciton migration into the trans segments.

B. Polydiacetylene - 4BCMU

Large areas of polydiacetylene (PDA) 4BCMU films with thicknesses between 100 to 800 nm were prepared by spin casting from solution onto sapphire substrates. Our TPRRS studies concentrate on the C=C stretching frequency in the PDA films. We recently reported cw resonant Raman scattering results for the same samples used in this TPRRS study. Primary results of the cw Raman study include that under pre-resonant excitation conditions with the laser photon frequency (ω_L) less than 1.95 eV, the entire inhomogeneously broadened phonon spectrum associated with C=C vibrations is observed in the Raman spectrum as a peak with a full width at half maximum (FWHM) of 60 cm^{-1}. In contrast, under resonant excitation (2 eV $< \omega_L <$ 2.4 eV) strong dispersion in the measured Raman shift as a function of ω_L varying from 1488 to 1529 cm^{-1} is observed. The measured dispersion is attributed to selective resonant excitation of different portions of the inhomogeneously broadened phonon profile, probably corresponding to a distribution of conjugation lengths.

Overall, the results demonstrate a strong coupling between measured vibrational frequencies and disorder-induced inhomogeneities in the exciton energy levels.

As in the case of $(CH)_x$ we also measured in TPRRS PDS $\Delta I < 0$ caused by photoexcitations bleaching of the RS cross section. However, a primary feature of the TPRRS spectra in PDA is the dramatic change in the measured linewidth as a function of pump irradiance. At a low irradiance of 5 MW/cm^2 the FWHM of the spectrum is approximately equal to that of the conventional Raman spectrum. As the irradiance increases to an intermediate level of 10 MW/cm^2, the FWHM decreases to a minimum value of 13 cm^{-1}. Increasing the irradiance above 10 MW/cm^2 gives rise to broadening of the FWHM until it reaches that of the cw Raman line at a strong irradiance of 21 MW/cm^2.

The narrowing of the TPRRS spectra can be thought of a spectral hole burning in the Raman profile analogous to hole burning in an absorption curve. To clarify the origin of the Raman spectral hole burning, we also measured the differential absorption, $\Delta\alpha$, of a probe beam scanned between 580 nm and 600 nm in the presence of a pump beam at 590 nm with a time delay of zero ps. The $\Delta\alpha$ curve, which arises from the electronic structure of PDA, reaches a minimum with the pump and probe wavelength equal to 590 nm and has a FWHM of 29 cm^{-1}. The correspondence between the pump and probe wavelengths (590 nm) to achieve the minimum linewidths for the TPRRS and $\Delta\alpha$ data suggests a direct relation between the phonon and electronic hole burning effects.

Lifetimes for the narrowed TPRRS spectra were also measured. With the pump and probe wavelengths at 590 nm, the hole widths broaden rapidly with a delay time of less than 10 ps for low level irradiances. As the irradiance increases from intermediate to strong, a delay time of greater than 10 ps and as much as 30 ps is required to observe significant broadening of the measured PRS profiles.

Since anti-Stokes Raman spectra are easily observed in PDS because of resonances associated with both the excitation and scattered wavelengths, we also examined the TPRRS behavior associated with the anti-Stokes spectrum. In contrast to the Stokes spectra, anti-Stokes TPRRS hole burning is not observed, and ΔI are positive rather than negative. Using resonant excitation with pump and probe wavelengths of 590 nm and a time delay of zero ps, the PRS $\Delta I/I$ increases linearly from +18% to +62% with total irradiances varying from 6.5 MW/cm^2 to 22.5 MW/cm^2. The decay of ΔI in anti-Stokes configuration can directly provide information on phonon lifetime measured through the phonon population decay. This is true since the AS signal is proportional to Δn--the change in phonon population, and thus its decay monitors the ultra phonon population relaxation processes.

Publications Acknowledging ONR Support

1. "Picosecond Photomodulation Spectroscopy of Conducting Polymers with a Nondegenerate Ground State" (with G.S. Kanner), J. Syn. Metals, in press.

2. "High Pressure Effects in Picosecond and cw Spectroscopy of Conjugated Polymers" (with B.C. Hess, G.S. Kanner and G.L. Baker), J. Syn. Metals, in press.

3. "Picosecond Lattice Dynamics in Conducting Polymer Thin Films" (with G.S. Kanner, B.C. Hess, L.X. Zheng and R.E. Benner), J. Syn. Metals **41**, 1391 (1991).

4. "Studies of Resonant Raman Scattering in Polydiacetylene Films" (with L.X. Zheng, R.E. Benner and G.L. Baker), J. Syn. Metals **41**, 235 (1991).

5. "Femtosecond Degenerate Four Wave Mixing Studies of $\chi^{(3)}$ in Conjugated Polymers" (with S.G. Han and K.S. Wong), J. Syn. Metals, in press.

6. "Picosecond Photomodulation Spectra of a-Si:H in the Small Signal Limit; Evidence for Transient PHotoinduced Electroabsorption" (with R.I. Devlen, G.S. Kanner and J. Tauc), Solid State Commun., in press.

7. "High Pressure Effects on Ultrafast Relaxation Kinetics of Excitons in Polydiacetylene 4BCMU" (with B.C. Hess, G.S. Kanner and G.L. Baker), Phys. Rev. Lett. **66**, (1991).

Final Report for the ONR FEL Contract No. N00014-90-J-1841
1/1/90 - 12/31/90
D.C. Mattis
Department of Physics
University of Utah

THEORY OF SOLIDS

Abstract

Several topics in condensed matter theory were pursued including disordered (amorphous) materials, thermodynamics and transport theory and high-temperature superconductivity.

Progress

In transport phenomena (electrical-, thermal-, mass-transport) the Boltzmann equation plays a key role; it is intermediate between a truly microscopic theory and a phenomenological (hydrodynamic) picture. We have achieved an exact solution of the time-dependent Boltzmann equation for electrical transport in semiconductors, in the presence of elastic scatterers, with or without additional inelastic scattering. Several surprises resulted: Ohm's law can be satisfied even if the distribution function cannot achieve steady state (the system heats up indefinitely, in the absence of thermal dissipation). We also examined the validity of several traditional approximations in this model by comparing with the exact solution. This work has also been confirmed and extended by J. Palmieri at the University of Illinois.

In theory of disordered and amorphous materials, we succeeded in extending the exactly *soluble theory* of disordered harmonic solids or liquids into the anharmonic regime. As a consequence, we have been able to formulate a theory of glass. Our model predicts a specific heat linear in temperature at low temperatures, a lack of atomic order, anomalous thermal transport, etc. At the date of this report, the work on glass was still in progress, but it will appear in the Ph.D dissertation of M. Molina and subsequent publications.

In connection with high-temperature superconductivity, we addressed the questions of transport of holes in two ways: (1) in CuO_2 planes, obtaining the transfer matrix elements of holes in the strongly interacting system by exact diagonalization of matrices up to $10^5 \times 10^5$ (see J. Phys. Cond. Matt. 1, 135 (1989)) and (2) in the Hubbard model, by a combination quantum-Monte-Carlo and variational technique, designed to obtain the dispersion of single holes accurately (Phys. Rev. B **42**, 6787 (1990)).

Finally, we addressed the question, how and why do the oxygen atoms line up in the basal planes of YBCuO materials? This issue is also related to the orthorhombic distortions of the crystal in the superconducting phase. The phase transition which occurs at some 900°C and causes orthorhombic distortion is connected with the uptake of oxygen in the basal planes of YBCuO, and correlates well with the T_c at which superconductivity sets in.

After a lengthy review of the literature, we discovered that despite many claims to the contrary, there was no good theory of this phenomenon and no explanations had been advanced which could quantitatively survive superficial scrutiny.

After examination of a number of options, we ultimately came to the following picture: there has to be substantial charge transfer from the basal planes into the CuO_2 planes as oxygen atoms line up, which implies a doping-dependent shift in the molecular bonding forces. Fortunately, there exists independent, corroborating *evidence* for this unusual phenomenon. Our paper reviewing the literature, analyzing the multiple phase

transitions, and advancing this new argument was submitted early in 1989 to the Journal Phase Transitions, and appeared in 1990.

Publications Acknowledging ONR Support

1. D.C. Mattis, A.M. Szpilka and Hua Chen, Mod. Phys. Lett. B3, 215 (1989).

2. D.C. Mattis, C.Y. Pan and H.-Q. Lin, J. Phys. Cond. Matt. 1, 135 (1989).

3. D.C. Mattis, M. Dzierzawa and X. Zotos, Phys. Rev. B 42, 6787 (1990).

4. A.M. Szpilka, M.L. Glasser, D.C. Mattis and M.P. Mattis, in *Phase Transitions* (Gordon and Breach), 22 (199), p. 185-209.